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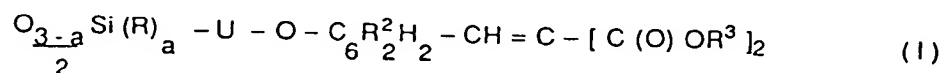
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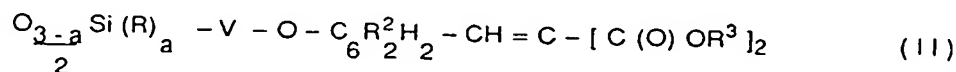
CH-4070 Basel (CH)

(54) Photostable cosmetic light screening compositions

(57) Photostable, cosmetic light-screening compositions comprise, in a cosmetically acceptable vehicle containing at least one fatty phase, about 0,5 to about 5 %, in particular about 1 to about 4 % by weight, of a dibenzoylmethane type UV-A screening agent and at least about 0,1 % to about 20 %, in particular about 0,5 to about 15% by weight, of a polymer UV-B filter of the benzylidene malonate silicone type comprising an organosiloxane having at least one unit of the general formula

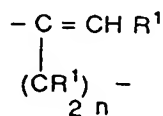


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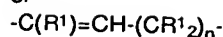


wherein

U is

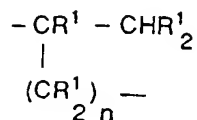


or



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and

V is $-\text{CR}^1_2-\text{CHR}^1-(\text{CR}^1_2)_n-$
or

any other units present in the said siloxanes being those represented by the general formula

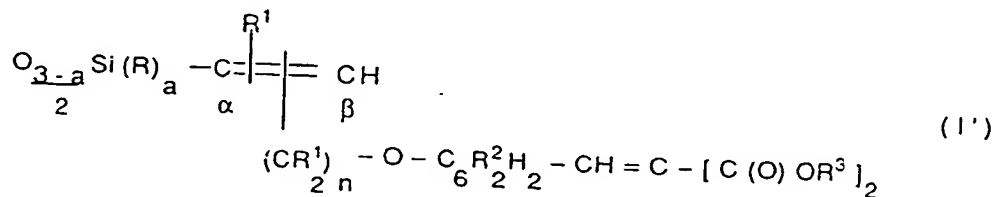


wherein R represents a C_{1-8} alkyl or an aryl group, R^1 is a hydrogen atom or a C_{1-5} alkyl group, R^2 is a hydrogen atom, a C_{1-5} alkyl group or a group OR^1 , R^3 is a C_{1-5} alkyl group, R'' represents a hydrogen atom, a monovalent C_{1-8} hydrocarbon or halogenated hydrocarbon group, a has a value of 0, 1 or 2, b has a value of 0, 1, 2 or 3 and n has a value of from 1 to 6, provided that the group $-\text{U}-\text{O}-$ or the group $-\text{V}-\text{O}-$ and the two R^2 groups are linked to the aromatic ring ($\text{C}_6\ldots$) at the para- and both meta-positions in relation to the group $-\text{CH}=\text{C}[\text{C}(\text{O})\text{OR}^3]_2$, the weight ratio of the silicone to the dibenzoylmethane derivative being not less than ca. 0.1, preferably not less than ca. 1.0 and not more than ca. 25, preferably not more than ca. 8 to 10.

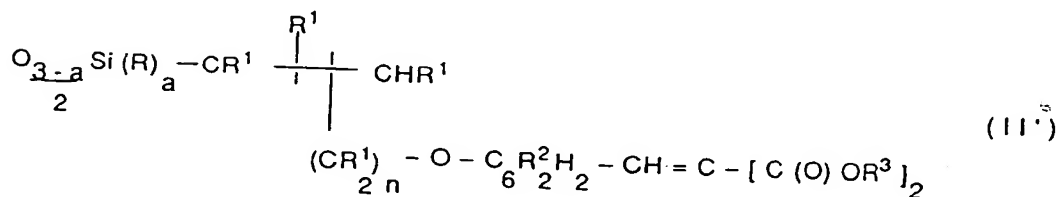
Description

The invention relates to photostable, cosmetic light-screening compositions for the protection of the human epidermis and the hairs against the ultraviolet rays of wavelengths between 290 and 400 nm.

In particular, it relates to such compositions which comprise, in a cosmetically acceptable vehicle containing at least one fatty phase, about 0,5 to about 5 %, in particular about 1 to about 4 % by weight, of a dibenzoylmethane type UV-A screening agent and at least about 0,1 % to about 20 %, in particular about 0,5 to about 15 % by weight, of a polymer UV-B filter of the benzylidene malonate silicone type exhibiting an organosiloxane having at least one unit of the general formula



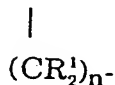
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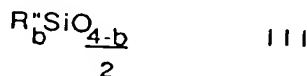
wherein the radical



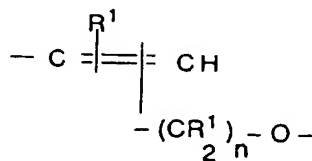
is either bound to the C_α atom and the radical



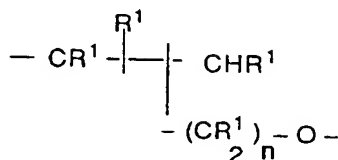
is bound to the C_β atom of the double bond in (I') or in the corresponding single bond in (II'), or vice versa, any other units present in the said siloxanes being those represented by the general formula



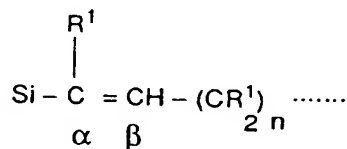
wherein R represents a C₁₋₈ alkyl or an aryl group, R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group, R'' represents a hydrogen atom, a monovalent C₁₋₈ hydrocarbon or halogenated hydrocarbon group, a has a value of 0, 1 or 2, b has a value of 0, 1, 2 or 3 and n has a value of from 1 to 6, provided that the



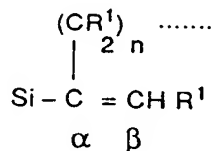
or the



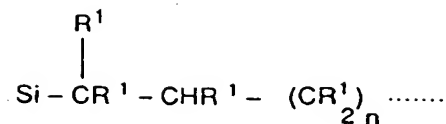
groups and the two R² groups are linked to the aromatic ring (C₆...) at the para- and both meta-positions in relation to the group -CH=C[C(O)OR³]₂, and the two vertical strokes designate either the alkylene derivative



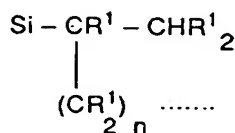
or the alkylidene derivative



in case of formula (I'),
or the saturated derivative with a linear chain



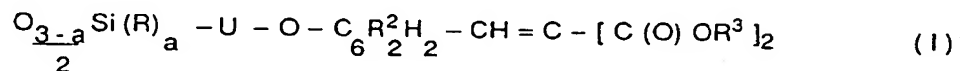
or the saturated derivative with a branched chain



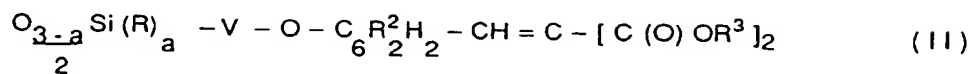
in case of formula (II'),

the weight ratio of the silicone to the dibenzoylmethane derivative being not less than ca. 0.1, preferably not less than ca. 1.0, and not more than ca. 25, preferably not more than ca. 8 to 10.

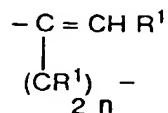
An alternative designation for the subject matter of compounds I' and II' is thus



or



wherein U is

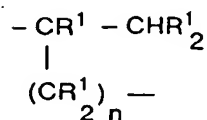


or

$-\text{C}(\text{R}^1) = \text{CH} - (\text{CR}^1_2)_n -$

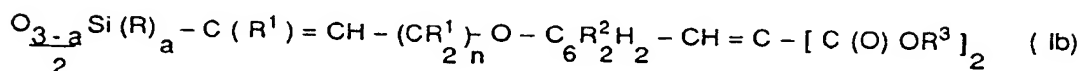
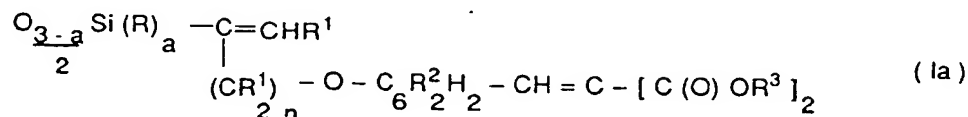
and

V is $-\text{CR}^1_2 - \text{CHR}^1 - (\text{CR}^1_2)_n -$



or

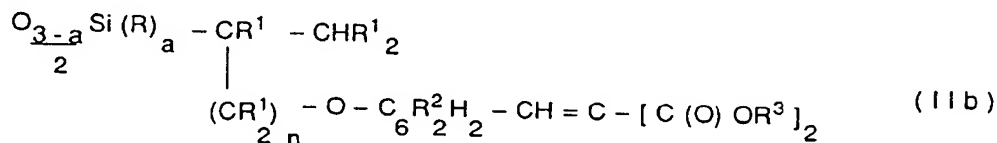
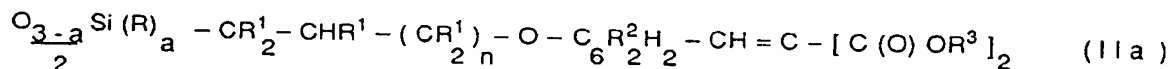
Formula I encompasses thus, as pointed out above, the alkylidene derivative Ia and the alkylene derivative Ib:



The preparation and the properties of these benzylidene malonate silicone types are described in WO 92/20690 of November 26, 1992.

The ratio of the alkylene to the alkylidene derivative is not critical at all, and is normally between ca. 5- ca. 50% : ca. 95-50% w/w.

Formula II encompasses the saturated linear (IIa) and saturated branched (IIb) derivatives:



The preparation and properties of these benzylidene malonate silicone types are described in EP 358 584 (USP 5053290) and FR 2 642 967-A1 (USP 5415854).

The suitable dimensions for the various parameters of the definition of the above captioned formula III are equally derivable from said WO publication. Thus, in the general formulae I and II the radicals can be defined as follows:

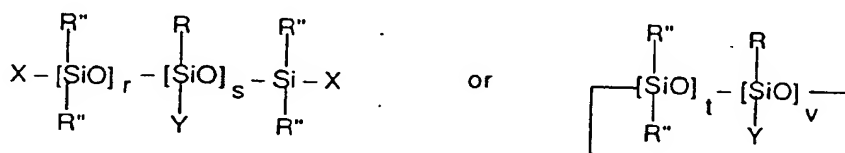
R may be for example methyl, ethyl, butyl or phenyl.

R¹ is hydrogen or a monovalent hydrocarbon or halogenated hydrocarbon group having up to 8 carbon atoms, for example alkyl, alkenyl, aryl, alkaryl, aralkyl and also halogen substituted alkyl, alkenyl, aryl, alkaryl and aralkyl are such groups. Particular examples include methyl, ethyl, vinyl, phenyl, tolyl, ethylphenyl, dimethylphenyl, benzyl, phenethyl and 3,3,3-trifluoropropyl, etc.

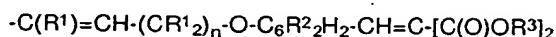
R³ denotes alkyl groups having up to 5 carbon atoms, as for example methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, isobutyl, pentyl and neopentyl, etc.

Examples for the C₁₋₅ alkyl radicals of R¹ and R² are as given above. Suitable radicals OR¹ are methoxy, ethoxy, propoxy, isopropoxy, etc. From the above listing, it can also be deduced that the alkyl and the alkoxy radicals may in the present context represent straight-chain and branched radicals.

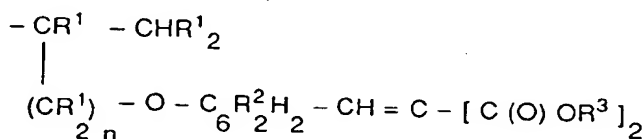
It is preferred that at least 80% of all R and R'' groups are methyl groups, most preferably substantially all R and R'' groups are methyl groups. It is also preferred that R¹ is either hydrogen, methyl or ethyl, most preferably hydrogen. Preferably each R² group is hydrogen or one R² group is a hydrogen, while the other one is an alkoxy group, preferably methoxy or ethoxy. R³ is preferably methyl or ethyl, a is preferably 1 while b is preferably 2, making the organosilicon compound a substantially linear or cyclic diorgano-siloxane polymer. However, if the diorgano-siloxane - see, e.g., Table 1, the second formula - is a substantially linear polymer at least two endblocking units must be present, thus requiring the presence of 2 units in which a has a value of 2, two units in which the value of b is 3 or one unit wherein a is 2 and one unit in which b is 3. n is preferably 1, 2 or 3. Suitable preferred polymers have therefore either the general formula



wherein R and R'' are as defined above, X denotes a group Y or a group R'' and Y denotes an alkylene group of the formula

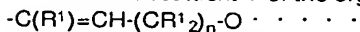


or the corresponding alkylidene derivative in case of formula (I), or, in case of formula (II), one of the groups -CR¹₂-CHR¹₂-(CR¹₂)_n-O-C₆R²₂H₂-CH=C-[C(O)OR³]₂, or

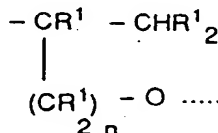


In the above captioned formulae, r has a value of from 0 to 130, s has a value of from 0 to 20, whereby at least one X denotes Y in the case that s=0; t has a value of from 0 to 10, v has a value of from 1 to 10 and v+t has a value of at least 3, and R¹, R² and R³ are as above.

In the substituent Y of the organosilicon compounds, the above captioned alkylene group

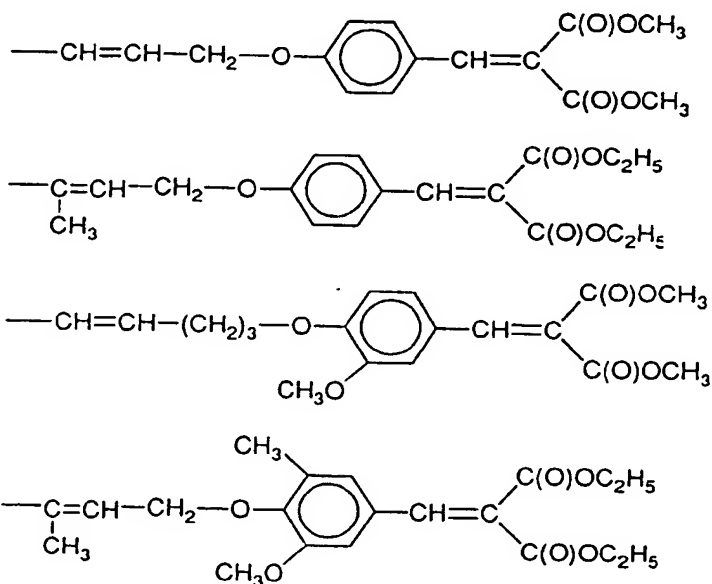


or the corresponding above captioned alkylidene derivative, or the groups

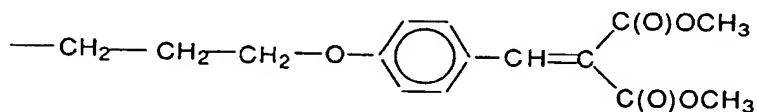


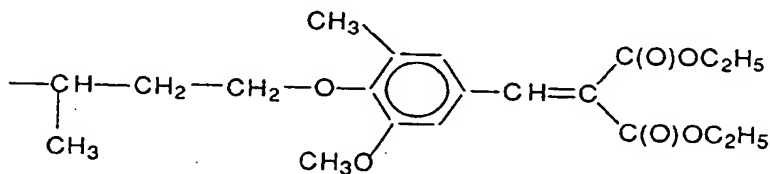
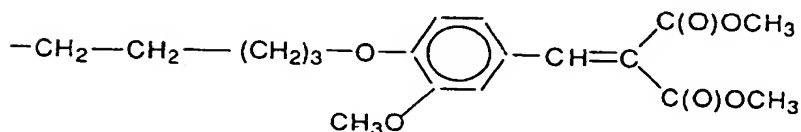
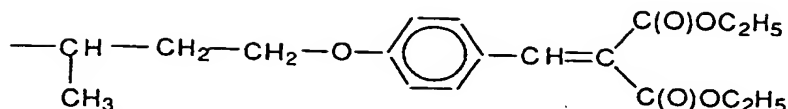
may occupy the meta-position or the para-position of the aromatic ring (C₆...) in relation to the group -CH=C[C(O)OR³]₂.

Preferably the para-position is thus occupied. The groups R^2 occupy the remaining two positions out of the para- and meta-positions in relation to the group $-\text{CH}=\text{C}[\text{C}(\text{O})\text{OR}^3]_2$. Examples of preferred substituents Y thus include

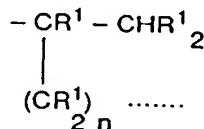


or the corresponding alkylidene derivatives, or the saturated linear structures, such as:





or the corresponding saturated branched derivatives, namely those carrying the structure



The material organosilicon compounds have at least one unit falling within the general formulae (I) or (II), preferably at least 2. Suitable organosilicon compounds are polymeric materials which may be homopolymers consisting only of such units (I) or (II), or they may be copolymers containing both units (I) or (II) and units having the general formula (III). The organosilicon compounds may vary from freely flowing liquids to highly viscous gum-like materials or resinous solids. Preferred, at least for cosmetic applications, are the liquid substantially linear organosiloxane homopolymers and copolymers, for example those having a viscosity (in c St) of from 100 to 20000mm²/s, more preferably 500 to 5000mm²/s as these are more easily mixed with other ingredients to make cosmetic compositions and as they will spread more easily onto the skin.

Organosilicon compounds which are especially preferred are those wherein the number of units (I) or (II) is limited to a maximum of 20% to 25% of the total number of siloxane units in the molecule. For maximum efficiency in its U.V. absorbing property it is preferred that the number of units (I) or (II) be limited to 10% to 12% or less of the total. The units of formula (I) or (II) may be distributed randomly in an organosiloxane polymer, they may be end-blocking units of the polymer or they may be located at the end of the polymer and pending in chain of the polymer at the same time. Units of the general formula (I) or (II) are conveniently situated at the end of the organosiloxane polymer forming one or more endblocking units of the polymer. In one class of the preferred organosilicon compounds which are substantially linear polyorganosiloxane polymers, both endblocking units have a structure represented by the general formula (I) or (II), while all other units are according to the general formula (III). The preferred organosilicon compounds have four units of the formula (I) or (II) and a larger number of units according to the general formula (III), e.g. 6 to 130, especially 8 to 80.

The organosilicon compounds are themselves effective in absorbing ultra violet radiation in the erythemic region (290 - 320nm) which makes them particularly suitable for use in cosmetic sunscreen preparations where absorption in

the UV-B region is particularly desirable. Most preferred for this application are those that have a maximum absorbance at 300 - 320nm.

As far as the UV-A light screen agent of the novel combinations is concerned, the preferred compound is 4-tert-butyl-4'-methoxydibenzoylmethane, as disclosed e.g. in USP 4 387 089 or CH-Patent 642 536.

Other suitable compounds of this particular type are: 2-methyl-dibenzoylmethane, 4-methyl-dibenzoylmethane, 4-isopropyl-dibenzoylmethane, 4-tert-butyl-dibenzoylmethane, 2,4-dimethyldibenzoylmethane, 2,5-dimethyldibenzoylmethane, 4,4'-diisopropyl-dibenzoylmethane, 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane, 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane, 2,4-dimethyl-4'-methoxydibenzoylmethane and 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

The function of the polymer filter containing formula I units is not only to provide the necessary so-called A + B total block in the final composition, in as far as the absorption of the UV-radiation is concerned, but also to photostabilize the involved UV-A screening agents, i.e. to guarantee a constant protection during prolonged exposure to the UV-light. This way, if a repeated application of the cosmetic formulation at various intervals is required, these intervals can be extended.

The present invention relates thus also to a process for stabilising dibenzoylmethane UV-A screening agents with respect to UV radiation of wavelengths between 290 and 400 nm, characterised in that 0,1 to 20 % by weight of the polymer filter is added to 0,5 to 5 % by weight of the dibenzoylmethane UV-A screening agent, the weight ratio of the silicone to the dibenzoylmethane derivative being not less than 0.1 and not more than 25.

The desired stabilization of the material UV-A filters is easily established by strictly parallel experiments with the respective UV-A filters and the novel combinations using an appropriately equipped Xenon lamp as a solar simulator. Irradiated are standard preparations of the investigated products, e.g. solutions in cosmetic solvents, the resulting sun-screen being spread on quartz plates. The stabilizing effect is directly correlated to the difference in absorbance at λ_{\max} before and after the irradiation. For an satisfactory effect, the structures of I and II are essential.

Even a slight variation of the structure in the molecules I and II leads to an unsatisfactory respective stabilization; under slight variation there is understood the "removal" of an ester group in I and II, thus resulting in cinnamates (namely the benzylidene acetates ---CH=C-C(O)OR^3), viz. EP 305059.

Both components of the present combination of the light-screening agents are lipophilic. The cosmetic formulations contain thus at least one fatty phase, and the formulations can consequently present themselves in the form of emulsions, lotions or gels.

Suitably the cosmetic screening composition takes the form of an oil, a lotion, a gel, a solid stick, an emulsion, e.g. cream, milk or of a vesicular dispersion of ionic or nonionic amphiphilic lipids, an aerosol, a spray, a foam, a powder, a shampoo, a hair conditioner or lacquer or a make-up, etc.

The usual solvents known to the skilled practitioner can be used for the preparation of these forms, e.g. oils, waxes, alcohols, polyols, etc. The preferred agents are fatty acids, esters, fatty alcohols, but also ethanol, isopropanol, propylene glycol, glycerine, etc.

The cosmetic formulations may contain further adjuvants, e.g. further solvents, thickeners, emollients, emulsifiers, humectants, tensides, preservatives, antifoams, fragrances, oils, waxes, lower polyols and monohydric alcohols, propellants, silicones, colourings and pigments, etc.

Other UV-B-filters may also be incorporated. Examples are given in USP 4 387 089 mentioned above. Particularly in case of emulsions, such UV filters may, naturally, also be water-soluble derivatives. As still further suitable UV-B filters, microfine pigments, such as the usual micropigments of metal oxides may be used.

In case of protection of the hairs, the suitable formulations are shampoos, conditioners, lotions, gels, emulsions, dispersions, lacquers, etc.

The preparation of all these formulations is well known to the skilled artisan in this field.

Examples of preferred polysiloxanes used for the present purpose are the ones of Table I below.

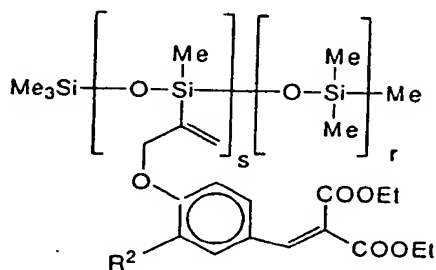
Further suitable polysiloxanes are those of Examples 3 to 6 of WO 92/20690, and also the product of Comparative Example 1 of WO 92/20690, the latter material representing a product encompassed by Formula II above.

Table I

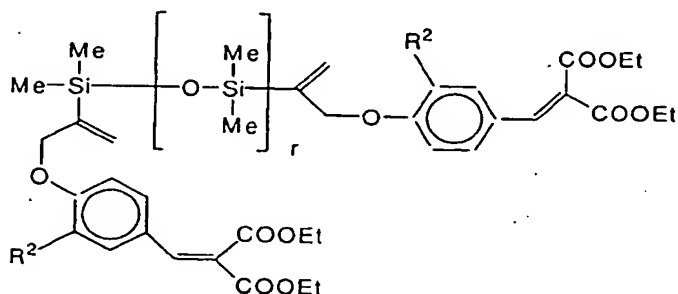
Illustrative Compounds and Formulae

The first column relates to the material Example of WO 92/20690 dealing with the preparation of products of this type.

| | | | | |
|----|---|------------|-------------|---|
| | 4 | s = ca. 4 | r = ca. 60 | R ² = H (most preferred, "Polysiloxane A") |
| | 4 | s = ca. 15 | r = ca. 127 | R ² = H |
| 15 | 4 | s = ca. 15 | r = ca. 116 | R ² = H |
| | 4 | s = ca. 11 | r = ca. 51 | R ² = H |
| | 4 | s = ca. 4 | r = ca. 60 | R ² = OMe |
| | 4 | s = ca. 15 | r = ca. 127 | R ² = OMe |
| 20 | 4 | s = ca. 15 | r = ca. 116 | R ² = OMe |
| | 4 | s = ca. 11 | r = ca. 51 | R ² = OMe |



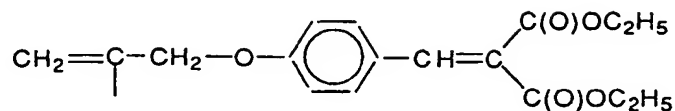
| | | |
|---|-----------|----------------------|
| 3 | r = ca. 7 | R ² = H |
| 3 | r = ca. 7 | R ² = OMe |



The above compounds contain ca. 20% of the alkylene isomers; their preparation can be illustrated as follows:

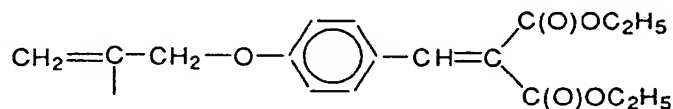
A. 39.84 g of [[4-(2-propynyloxy)phenyl]methylene]-diethyl ester were dissolved in 100 g of toluene and heated under nitrogen to about 70°C. 39.96 g of a hydrosiloxane having a degree of polymerisation of 8 and 25 mpc (mole %) SiH groups (9.7% SiH) were then added dropwise after a platinum complex was also added, giving 10⁻⁴ mole of Pt per mole of SiH of the hydrosiloxane. The mixture was heated to reflux and maintained until all SiH had disappeared of the infrared spectroscopic analysis. It was then allowed to cool to room temperature. The toluene was then evaporated to leave after washing 60.5 g of a brown, viscous polymer having the average structure R⁴.

$[(CH_3)_2SiO]_8-R^4$, wherein R has the formula



Only 0.34% by weight of the total reaction product of unreacted [[4-(2-propynyloxy)phenyl]methylene]-diethyl ester was present in the end product.

B. 13.28 g of [[4-(2-propynyloxy)phenyl]methylene]-diethyl ester were dissolved in 75 g of toluene and heated under nitrogen to about 70°C. 44 g of a hydrosiloxane having a degree of polymerisation of 65 and 6 mpc SiH groups (2.36% SiH) were then added dropwise after a platinum complex was also added, giving 10^{-4} mole of Pt per mole of SiH of the hydrosiloxane. The mixture was heated to reflux and maintained until all SiH had disappeared of the infrared spectroscopic analysis. It was then allowed to cool to room temperature. The toluene was then evaporated to leave after washing 52 g of a brown, viscous polymer having the average structure $(CH_3)_3SiO-[(CH_3)_2SiO]_{59}-[(CH_3)R^4SiO]_4-Si(CH_3)_3$ wherein R^4 has the formula



("Polysiloxane A").

Examples

1. A sunscreen cream is prepared with the following ingredients:

| A) | % (w/w) |
|---|---------|
| Stearic acid (octadecanoic acid) | 10.0 |
| Butylmethoxy dibenzoylmethane (1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)-1,3-propanedi-one) (sold under the trade name PARSOL 1789 by Givaudan-Roure S.A.) | 2.0 |
| Glyceryl mono myristate (tetradecanoic acid ester with 1,2,3-propanetriol) Cetyl alcohol ((hexadecanol) | 5.02.0 |
| Coco-caprylate/caprate (Mixture of esters of coconut alcohol and n-octanoic acid and n-decanoic acid) (sold under the trade name CETIOL LC by Henkel) | 10.0 |
| Polysiloxane A | 10.0 |
| Dea Cetylphosphate (Diethanolamine salt of hexadecyl phosphate) (sold under the trade name AMPHISOL by Givaudan-Roure S.A.) | 3.0 |
| EDTA Na ₂ (disodium ethylenediamine tetra acetic acid) | 0.1 |
| B | |
| Deionized water | 51.0 |
| Propyleneglycol (1,3-propanediol) | 6.0 |
| Mixture of parabens in phenoxyethanol (Mixture of methyl, ethyl, propyl and butyl esters of 4-hydroxy benzoic acid) (sold under the trade name Phenonip® by Nipa Laboratoires Ltd.) | 0.6 |
| C | |
| Conventional fragrance | 0.3 |

2. A sunscreen lotion is prepared with the following ingredients:

| | |
|--|---------|
| A | % (w/w) |
| Glyceryl mono myristate | 5.0 |
| Cetyl alcohol | 2.0 |
| Butylmethoxy dibenzoylmethane | 1.0 |
| Isopropyl myristate (2-methylethyl tetradecanoate) | 7.0 |
| Oleyl alcohol (octadecanol) | 3.0 |
| Polysiloxane A | 5.0 |
| Dea Cetylphosphate | 3.0 |
| EDTA Na ₂ | 0.1 |
| B | |
| Deionized water | 67.0 |
| Propyleneglycol | 6.0 |
| Mixture of parabens in phenoxyethanol | 0.6 |
| C | |
| Fragrance | 0.3 |

3. A sunscreen lotion is prepared with the following ingredients:

| A | % (w/w) |
|---|---------|
| Glyceryl mono stearate | 4.0 |
| Butylmethoxy dibenzoylmethane | 1.0 |
| Cetyl alcohol | 1.0 |
| Coco-caprylate/caprate | 6.0 |
| Polysiloxane A | 10.0 |
| Potassium cetyl phosphate (potassium salt of hexadecyl phosphate) (sold under the trade name AMPHISOL K by Givaudan-Roure S.A.) | 2.0 |
| EDTA Na ₂ | 0.1 |
| B | |
| Deionized water | 59.36 |
| Carbomer (1% dispersion in water, homo polymer of acrylic acid crosslinked with an allyl ether of sucrose) (sold under the trade name Carbopol 981® by B.F. Goodrich) | 10.0 |
| Propyleneglycol | 5.0 |
| Potassium hydroxide, 10% solution | 0.64 |
| Mixture of parabens in phenoxyethanol | 0.6 |
| C | |
| Fragrance | 0.3 |

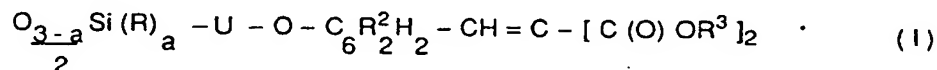
4. A water in silicone cream (a W/O formulation) is prepared with the following ingredients:

| A | % (w/w) |
|---|---------|
| Butylmethoxy dibenzoylmethane | 1.0 |
| C _{12/15} alkyl benzoate (mixture of dodecyl & pentadecyl benzoate) (sold under the trade name FINSOLV TN by Finetex Corp.) | 5.0 |
| Silicone oil (copolyol of dimethicone and cyclomethicone) (sold under the trade name DC-3225 by Dow Corning) | 10.0 |
| Silicone oil (mixture of cyclomethicone and dimethiconol) (sold under the trade name DC-1401 by Dow Corning) | 10.0 |
| Polysiloxane A | 10.0 |
| EDTA Na ₂ | 0.1 |
| B | |
| Deionized water | 56.0 |
| Sodium chloride | 4.0 |
| Propyleneglycol | 3.0 |
| Mixture of parabens in phenoxyethanol | 0.6 |
| C | |
| Fragrance | 0.3 |

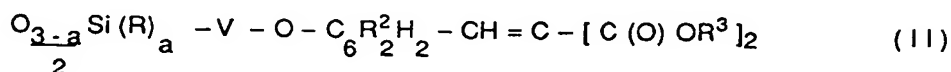
In the same way, the Polysiloxane A can be replaced in the above formulations by the Compound of Comparative Example 1 of WO 92/20690.

Claims

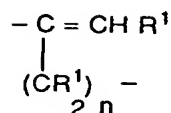
1. Photostable, cosmetic light-screening composition, characterised in that it comprises, in a cosmetically acceptable vehicle containing at least one fatty phase, about 0,5 to about 5 %, in particular about 1 to about 4 % by weight, of a dibenzoylmethane type UV-A screening agent and at least about 0,1 % to about 20 %, in particular about 0,5 to about 15% by weight, of a polymer UV-B filter of the benzylidene malonate silicone type comprising an organosiloxane having at least one unit of the general formula



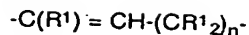
or



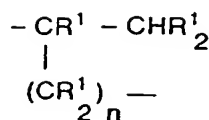
wherein
U is



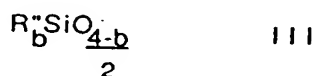
or



and



any other units present in the said siloxanes being those represented by the general formula



wherein R represents a C₁₋₈ alkyl or an aryl group, R¹ is a hydrogen atom or a C₁₋₅ alkyl group, R² is a hydrogen atom, a C₁₋₅ alkyl group or a group OR¹, R³ is a C₁₋₅ alkyl group, R'' represents a hydrogen atom, a monovalent C₁₋₈ hydrocarbon or halogenated hydrocarbon group, a has a value of 0, 1 or 2, b has a value of 0, 1, 2 or 3 and n has a value of from 1 to 6, provided that the group -U-O- or the group -V-O- and the two R² groups are linked to the aromatic ring (C₆...) at the para- and both meta-positions in relation to the group -CH=C[C(O)OR³]₂, the weight ratio of the silicone to the dibenzoylmethane derivative being not less than ca. 0.1, preferably not less than ca. 1.0 and not more than ca. 25, preferably not more than ca. 8 to 10.

2. A composition according to Claim 1, wherein the ratio of the alkylene to the alkylidene derivative is ca. 5 - 50 : ca. 95-50 % w/w, in particular ca. 20-30 : 80-70% w/w, or in case of the saturated derivatives, the linear derivatives is the predominant derivative.
3. A composition according to Claim 1 or 2, wherein at least 80% of all R and R'' groups of (I) or (II) are methyl groups.
4. A composition according to Claim 1, 2 or 3, wherein each R¹ of (I) is selected from hydrogen, methyl and ethyl.
5. A composition according to anyone of the preceding claims, wherein at least one R² group of (I) or (II) is hydrogen, the other being hydrogen, methoxy or ethoxy.
6. A composition according to anyone of the preceding claims, wherein R³ of (I) is methyl or ethyl.
7. A composition according to anyone of the preceding claims, wherein each R¹ and R² group of (I) or (II) is hydrogen.
8. A composition according to anyone of the preceding claims, wherein the polymer of I and II are substantially linear or cyclic diorganosiloxane polymers.
9. A composition according to anyone of the preceding claims, wherein the group U-O- or the group V-O- occupy the para-position on the aromatic ring in relation to the group -CH=C[C(O)OR³]₂, and both groups R² occupy the meta-positions on the aromatic ring in relation to the group -CH=C[C(O)OR³]₂.

10. A composition according to anyone of the preceding claims, wherein the number of units of (I) or (II) are limited to a maximum of ca. 20% to ca. 25% of the total number of siloxane units in the molecule.
- 5 11. A composition according to anyone of the preceding claims, wherein the number of units of (I) or (II) are limited to ca. 10% to ca. 12% or less of the total number of units.
12. A composition according to anyone of the preceding claims, wherein units of the general formula (I) or (II) are situated at the end of the organosiloxane compound.
- 10 13. A composition according to anyone of the preceding claims, wherein the polysiloxane of I or II has four end-blocking units of formula (I) or (II) and from 6 to 130 units of the general formula (III).
14. Composition according to anyone of the preceding claims, characterised in that the dibenzoylmethane derivative is selected from the following compounds: 2-methyldibenzoylmethane, 4-methyl-dibenzoyl-methane, 4-isopropyl-
15 dibenzoylmethane, 4-tert-butyl-dibenzoyl-methane, 2,4-dimethyldibenzoylmethane, 2,5-dimethyldibenzoylmethane, 4,4'-diisopropyldibenzoylmethane, 4-tert-butyl-4'-methoxydibenzoylmethane, 2-methyl-5-isopropyl-4'-methoxy-
dibenzoylmethane, 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane, 2,4-dimethyl-4'-methoxydibenzoylmethane and 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.
- 20 15. Composition according to anyone of the preceding claims, characterised in that the dibenzoylmethane derivative is 4-tert-butyl-4'-methoxydibenzoylmethane.
16. Composition according to anyone of the preceding claims, characterised in that it takes the form of an oil, a lotion, a gel, a solid stick, an emulsion e.g. cream, milk or of a vesicular dispersion of ionic or nonionic amphiphilic lipids,
25 an aerosol, a spray, a foam, a powder, a shampoo, a hair conditioner or lacquer or a make-up.
17. Composition according to anyone of the preceding claims, characterised in that it contains, in addition, cosmetic adjuvants selected from solvents, thickeners, emollients, emulsifiers, humectants, tensides, preservatives, anti-
30 foams, fragrances, oils, waxes, lower polyols and monohydric alcohols, propellants, silicones, colourings and pigments.
18. Composition according to anyone of the preceding claims, characterised in that it contains, in addition, (a) further water-soluble or lipophilic UV screening agent(s).
- 35 19. Process for a cosmetic treatment of the human epidermis or the hairs in view of its protection against UV radiation of wavelengths between 290 and 400 nm, characterised in that it consists in applying to the skin or the hairs an effective quantity of a cosmetic screening composition as defined in anyone of Claims 1 to 18.
- 40 20. Process for stabilising dibenzoylmethane UV-A screening agents with respect to UV radiation of wavelengths between 290 and 400 nm, characterised in that 0,1 to 20 % by weight of the polymer filter defined in Claim 1 is added to 0,5 to 5 % by weight of the dibenzoylmethane UV-A screening agent, the weight ratio of the silicone to the dibenzoylmethane derivative being not less than 0.1 and not more than 25.
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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 6022

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| D,A | WO-A-92 20690 (GIVAUDAN-ROURE S.A.) 26 November 1992 * the whole document * | 1-19 | A61K7/42 |
| A | WO-A-93 10745 (L'OREAL) 10 June 1993 * example 4 * | 1-19 | |
| A | FR-A-2 642 967 (L'OREAL) 17 August 1990 * the whole document * | 1-19 | |
| A | EP-A-0 305 059 (DOW CORNING LIMITED) 1 March 1989 * the whole document * | 1 | |
| A | EP-A-0 383 655 (L'OREAL) 22 August 1990 * the whole document * | 1 | |
| The present search report has been drawn up for all claims | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | A61K |
| Place of search THE HAGUE | | Date of completion of the search 19 February 1996 | Examiner Couckuyt, P |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background U : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | |

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